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ANNULAR DENUDER RESULTS FROM BOISE, ID

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16. ABSTRACT

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Samples from annular denuder systems (ADS) collected during the winter of 1986-1987 in Boise, ID have been analyzed for HNO_2, SO_2, HNO_3, $SO_4^=$ NO_3^- content. The correlations between the data from the ADS and XRF measurements of Pb and K in the fine particles were examined to determine if any of the species collected by the ADS (eg HNO_2, HNO_3) would serve as receptor modeling tracers for the extractable organic matter (EOM) from mobile and/or woodburning sources. Results of these correlations will be discussed. This report also discusses the precision of the ADS measurements and compares results obtained with other measuring methods for similar species (eg XRF data for S with $SO_4^=$ measured with the ADS). In addition, comparison of ambient concentrations of species measured with the ADS at the two monitoring sites in Boise will also be examined in relationship to the chemical properties of fine particles collected in Boise, ID and spatial homogeneity of gases and aerosols. Some comparisons are also made with ADS data collected in Denver and Research Triangle Park, NC.

INTRODUCTION

The Annual Denuder Method (ADM)[1] was used in the Integrated Air Cancer Project field sampling program in Boise, ID to obtain 12 hour air quality data on the concentrations of HNO_2, SO_2, HNO_3, sulfate and nitrate at the two main monitoring sites. The ADM data will be used to determine the relative spatial homogeneity of the atmosphere between monitoring sites and obtain data to correlate concentrations of condensable nitroaromatic compounds with HNO_2 and HNO_3. The assumption is that these inorganic gas phase nitrogenous species may be the nitrating agents that produce nitroaromatic particles in the atmosphere.

We will discuss in this report recent developments in sampling and analysis of atmospheric aerosols and gases using the ADM. We also discuss how modifications in the annular denuder system may be used to obtain reliable measurements for HNO_2 and HNO_3 and how HNO_2 may cause chemiluminescent NO_2 measurements to be overestimated.

EXPERIMENTAL

Site Descriptions

Boise, ID. During winter of 1986-1987 air quality data and samples were collected at two primary monitoring sites as part of the Environmental Protection Agency's (EPA) Integrated Air Cancer Project. One site was located in a city park (Elm Grove Park) in a residential neighborhood impacted by wood smoke emissions from numerous single family dwellings. The second primary site (Fire Station) was on top of a fire station adjacent to a major intersection. This site was used to examine the chemical characteristics of primary emission from vehicles.

Research Triangle Park, NC (RTP). During the winter of 1987-1988 experiments were performed with annular denuders on the roof of the EPA Annex. These experiments were performed to test the effect of denuder coatings on the collection of HNO_3, HNO_2 and SO_2.

Sampling Schedule. Annular denuder and aerosol samples were collected in Boise primarily over 12 hour sampling periods beginning at 7 AM and 7 PM in order to capture daytime and nighttime conditions. The sampling schedule at the RTP site was typically 20-22 hour periods from 10 AM to 9 AM.

Inlet-Annular Denuder-Filter Pack Configuration

A coarse particle elutriator-impactor inlet rendered inert by a Teflon coating was the primary inlet assembly used in these ADM studies. Figure 1 shows the inlet-denuder-filter pack arrangement used in Boise. A 47 mm Nylosorb membrane filter followed the Teflon filter, to collect HNO_3 produced from the disassocaition of NH_4NO_3 particles originally collected on the Teflon filter. The inlet design, denuder coating extraction and analysis methods, and operational procedures have been described by Vossler et al.[1] In the study at RTP, the denuders and impactor inlet were modified to incorporate a replaceable fritted glass impactor surface coated with either Dow Corning oil or mineral oil to prevent bounce of large particles into the denuders. This modification is shown in Figure 1. The impactor inlet d_{50} cutpoints were 2.5 µm at the flow rates used in Boise and 2.1 µm for the RTP study.

The objective of the experiments performed in RTP was to decouple the collection of HNO_3 from HNO_2 by coating the first annular denuder with a 0.2% solution of NaF. Three rather than two denuders were used, where denuders 2 and 3 were coated with Na_2CO_3. In this configuration all HNO_3 is collected on the NaF denuder and HNO_2 is only collected on the Na_2CO_3 denuders. Results and implications of this denuder arrangement are discussed later in this report.

Summary of Sampling and Analysis Methods

Table I lists samplers and instruments used to obtain data on the concentrations of major inorganic gases and aerosols in Boise and RTP. The annular denuders were extracted in 15 ml of distilled water and stored in a refrigerator in sealed plastic bottles. Extracts and filters were shipped to EPA, Research Triangle Park, NC and stored in a refrigerator prior to anlaysis. Filters from the ADM were sealed in plastic petri dishes and stored in a refrigerator with the denuder extracts. The filters were extracted in 10 ml Ion Chromatographic (IC) Na_2CO_3 buffer solution in an ultrasonic bath just prior to IC analysis for NO_2^-, NO_3^- and $SO_4^=$ content.

RESULTS

Annular Denuder and Related Gas-Aerosol Data

Figure 2 is a summary of the means of daytime(AM) and nighttime(PM) data for HNO_2, SO_2, HNO_3, $SO_4^=$, NO_3^-, NO_x and mass for samples collected at the Elm Grove Park and Fire Station primary sites in Boise. The samples were collected between November 8, 1986 and February 2, 1987 and represent 30% of the samples collected in Boise. The complete set of results from the ADM will be reported elsewhere. These samples were collected to assist in receptor modeling studies to determine the origin of extractable organic matter (EOM) and the origin of mutagenic properties of the EOM. For this wintertime study nitric acid was typically less than 0.5 $\mu g/m^3$ while particle nitrate averaged 5 $\mu g/m^3$. This contrasts with summertime studies in the Eastern U.S. where nitric acid is typically 2 to 3 times the fine particle nitrate concentrations.[1]

Table II is a summary of the correlation statistics for data collected with the ADM systems, CO and NO_x monitors and dichotomous samplers operated at the two main monitoring sites in Boise. These correlations between key chemical air pollutant species serve as one means of evaluating and comparing air quality between the Fire Station and Elm Grove Sites in Boise. Also these correlations are used in identifying chemical species which may serve as candidates for use as tracers for receptor modeling calculations. For example, the moderately high correlation between Pb and CO suggests CO may be a useful surrogate for Pb as a tracer for mobile source emission in receptor modeling calculations.

Table III shows selected ADM results from the Elm Grove Site in Boise. These data are presented to provide information on the relative daytime-nighttime concentrations of gases and aerosols and show the variability in the amount of nitrate that evaporates from the ADM Teflon filters.

Precision and Accuracy of Sampling and Analysis Procedures

Two factors which are considered in estimating the precision of measurements obtained with the denuder system are flow rate variations and precision of IC analysis. In the ADM study reported by Vossler et al[1] paired samples had average differences for the measurement of SO_2, HNO_3, and HNO_2 of 3.4%, 6.4% and 8.3%. These rather small deviations were due mainly to variations in sampling flow rate of the paired assemblies and ion

chromatography analysis. Typically variations were less than ± 5% for flow and less than ± 3% for IC analysis. For our studies in Boise and RTP, NC the IC analysis precision for $SO_4^=$, NO_3^-, NO_3^-, NO_3^- was typically better than ± 2%, and flow rates were maintained to ± 5%.

Sulfur-Sulfate Relationship

In Boise fine particle samples were collected with dichotomous samplers to obtain mass and elemental composition data by XRF procedures for use in receptor model calculations. The mass ratio of fine particle sulfate concentrations measured with the ADM to the sulfur measured from the dichotomous sampler by XRF for samples collected at both main monitoring sides in Boise was $SO_4^=$ (ADM)/S(XRF) = 2.99 ± 0.24 at the 95% confidence limits. This is in close agreement to the $SO_4^=$/S data obtained by Lewis et al[2] in a wintertime, 1982, receptor modeling study in Denver. The ratio of 3.00 corresponds to all sulfur being in the form of sulfate. Figure 3 is a weighted least squares plot of $SO_4^=$ versus the S in fine particles sampled in Boise. In the weighted least squares calculation[3] the regression line was forced through zero and data weighted so that the variance of Y ($SO_4^=$ concentration) was proportional to X^2 (X = S concentration). Thus the best estimate of the regression coefficient is the average of n slopes obtained from each pair of observations Y_i/X_i. A number of data points are below the best straight line fit of the data for sulfur concentrations >1.2 μg m^{-3}. This suggests the data may exist in two modes. Additional samples are being analyzed to determine whether this is real or due to other factors such as incomplete extraction of the $SO_4^=$ due to elevated concentrations of extractable organic matter present on the filters.

DISCUSSION

For studies performed in Boise and a previous Denver receptor study performed in 1982[2], a number of similarities in air quality data were observed. For example, the mean concentration of nitrate in Boise was typically 13% of the fine particle mass (Figure 2). In the previous wintertime study in Denver[2] nitrate represented 14% of the daytime fine particle mass.

In Boise, HNO_2 concentrations averaged nearly 10% of the NO_2 values. Even during the day HNO_2 averaged 7% of the NO_2 concentration. During summer, HNO_2 daytime concentrations are typically less than 1 μg/m^3. However, during winter, cold and cloudy conditions tend to reduce the photo-disassociation of HNO_2, which may account for a mean daytime concentration of HNO_2 of 3 μg/m^3, observed in Boise (Figure 3). In addition, it should be noted that chemiluminescent NO_x monitors respond to HNO_2 just as it responds to NO_2. Therefore, NO_2 measurements in Boise or any other urban area would tend to be overestimated due to the positive interference from HNO_2. This, in turn, would require adjustment in chemiluminescent NO_2 data. For example on January 14, 1987 the average daytime HNO_2 concentration was 4.3 μg/m^3, which was 9.5% of the NO_2 concentration. Therefore the average daytime NO_2 concentration was really 41 μg/m^3 rather than the 45 μg/m^3 measured by the chemiluminescent NO_x monitor.

Figure 2 shows data that indicate that SO_2, nitrate, fine article mass and sulfate mean concentrations were nearly identical for data collected at the two primary monitoring sites in Boise. This is an important observation, if calculations on pollutant exposure are to be performed using the data from the two primary monitoring sites.

To improve the reliability of HNO_3 and HNO_2 data obtained with the

annular denuder, a modification of the annular denuder coating procedure was tested. In previous annular denuder studies some oxidation of HNO_2 to nitrate on the denuder surface during sampling was possible during summertime conditions. Recently Febo et al[4] reported on the use of a NaCl coated denuder followed by Na_2CO_3 denuders to decouple the collection of HNO_3 from HNO_2. In this configuration only HNO_3 (and some SO_2) is collected on the NaCl coated denuder, and HNO_2 is collected on the Na_2CO_3 denuder. Thus if HNO_2 is oxidized on the Na_2CO_3 denuder there would be no interference with HNO_3 measurements since the HNO_3 had been removed by the NaCl coated denuder. In our laboratory we choose to use a NaF coated denuder instead of the NaCl because the Cl^- peak tended to obscure the NO_2^- and NO_3^- peaks during ion chromatographic analysis of the denuder extract. In our studies the first denuder is coated with a 50:50 water:methanol solution containing 0.2% NaF and 0.2% glycerine using a procedure described by Vossler et al.[1]. The NaF coated denuder collects 99% of the HNO_3 and some SO_2 at a flow rate of 10 L/minute. The amount of SO_2 collected on the NaF denuder appears to depend on relative humidity. There was no evidence of HNO_2 collection on the NaF coated denuder. The HNO_2 and balance of the ambient concentrations of SO_2 are found on the first Na_2CO_3 denuder. These preliminary studies suggest the annular denuder system using a NaF coated denuder followed by two Na_2CO_3 coated denuders eliminates the potential problem of HNO_2 interfering with HNO_3 measurements due to oxidation of NO_2^- to NO_3^- on the denuder.

SUMMARY

Annular denuder and related air quality data collected in Boise, ID as part of the EPA Integrated Air Cancer indicated fine particle nitrate to be a major fraction (13%) of fine particle mass, while sulfate represented 5% of fine particle mass. Nitrous acid concentrations averaged 10% of NO_2 concentration and would produce a significant interference with chemiluminescent NO_2 determinations. Annular denuder data showed substantial evaporation of fine particle nitrate occurs from Teflon filters even during wintertime conditions. This suggests filter pack measurements of nitrate and HNO_3 may have substantial uncertainties. Introduction of a NaF annular denuder between the inlet and a Na_2CO_3 denuder eliminates the potential interference of HNO_2 with HNO_3 measurements and improves the annular denuder method as a tool to measure gas and aerosol phase oxides of nitrogen.

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Table I. Samplers and Analysis Procedures Used in Boise Study

Sampler/Analyzer	Flow Rate L min^{-1}	Species*	Ref.
Annular Denuder Method (ADM) (Boise, ID)	15	SO_2, NO_3^-, $SO_4^=$, HNO_2 HNO_3	1
Annular Denuder Method (ADM) (RTP, NC)	10	SO_2, HNO_3, HNO_2, NO_3^-, $SO_4^=$	1
Anderson Inc. Dichotomous Sampler	16	Mass, Elemental	2
Monitor Laboratories Chemiluminescent NO_x Analyzer	1	NO, NO_2, NO_x	2
Beckman Gas Cell CO Monitor	1	CO	2

*47 mm Gelman Teflon filters followed by 47 mm Nylasorb filters were used with the ADM system; ADM system fabricated by University Research Glassware, Carrboro, NC. A pair of 37 mm Gelman Teflon filters was used to collect particles with the dichotomous sampler.

Table II. Summary of Correlation Statistics for Gas and Aerosol Samples Collected in Boise, ID

Species (Site)	N	AM	N	PM	N	Overall
HNO_2 vs NO_2 (EGP)	19	0.700	25	0.564	44	0.552
HNO_2 vs NO (EGP)	19	0.570	25	0.634	44	0.529
HNO_2 vs NO_2 (FS)	17	0.381	22	0.634	39	0.375
HNO_2 vs NO (FS)	17	0.610	22	0.858	39	0.557
Pb vs CO (EGP)	20	0.718	23	0.643	43	0.682
Pb vs CO (FS)	18	0.920	24	0.744	42	0.835

AM refers to data collected between 7 AM and 7 PM, PM refers to data collected between 7 PM and 7 AM.

Table III. Annular Denuder Method Data for Boise

DATE SAMPLED	TIME	Concentration, μg m^{-3} GASES HNO_2	HNO_3	SO_2	PARTICLES NO_3^-	$SO_4^=$	% Nitrate Found on Nylon Filter
12-6-86	night	6.95	0.0	5.40	1.68	1.16	30
12-7-86	day	2.00	0.25	2.55	2.40	2.04	81
12-7-86	night	5.35	0.03	6.66	1.46	1.88	25
12-9-86	night	3.29	0.16	10.53	3.05	1.39	56
12-10-86	night	3.83	0.12	9.66	4.32	2.12	26
12-11-86	day	1.37	0.34	7.60	4.70	2.08	40
12-11-86	night	7.52	0.09	12.03	4.46	2.91	14
12-12-86	day	2.79	0.20	10.62	4.14	2.41	29

Samples were collected between 7AM-7M (day period) and 7PM-AM (night Period)

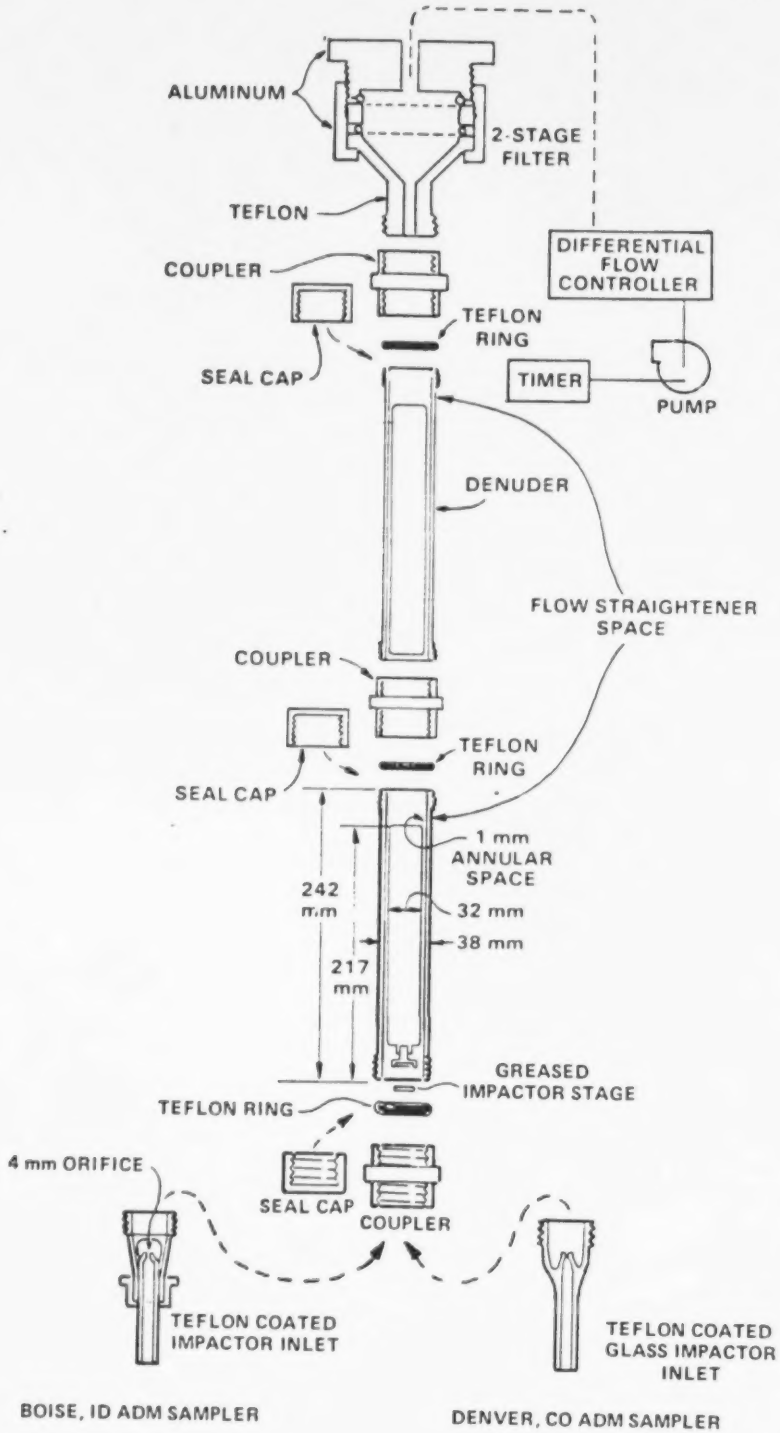

Figure 1 - Diagram of annular denuder systems used in the Boise, ID EPA's Integrated Air Cancer Project and Denver Air Toxic Study.

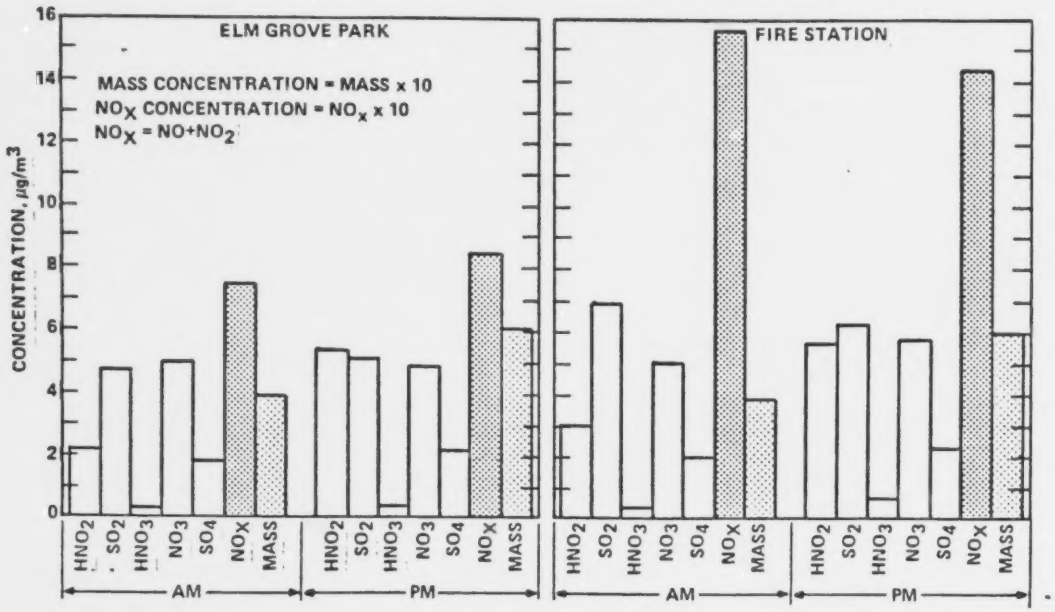

Figure 2 - Means of AM and PM measurements at the main monitoring sites in Boise, ID during the winter of 1986 and 1987.

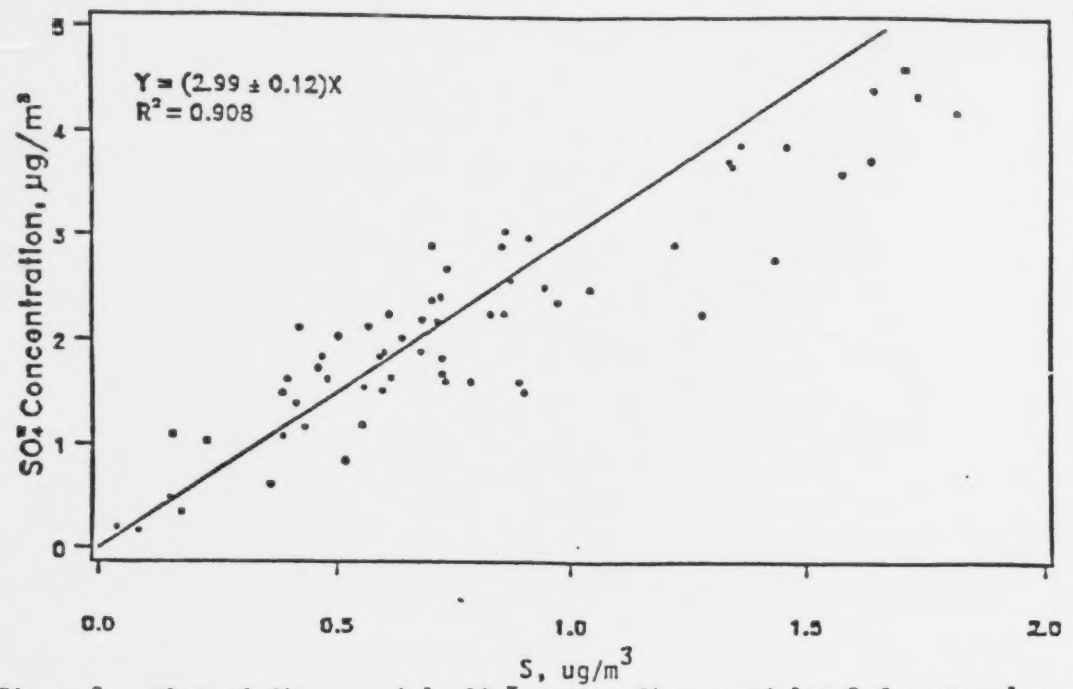

Figure 3 - Plot of fine particle $SO_4^=$ versus fine particles S from samples collected in Boise IACP study.